



**PATENT APPLICATION**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Ulrich GERBER et al.

Group Art Unit: 1796

Application No.: 10/552,482

Examiner: A. ADMASU

Filed: December 7, 2006

Docket No.: 125198

For: MANNICH BASES AND PROCESSES FOR THE PREPARATION OF MANNICH BASES

**DECLARATION UNDER 37 C.F.R. §1.132**

I, Ulrich GERBER, a citizen of Switzerland, hereby declare and state:

1. I have a degree in Chemistry which was conferred upon me by Höhere Technische Lehranstalt HTL Winterthur (now Zürcher Fachhochschule (Zurich University of Applied Sciences (ZHAW)) in Winterthur, Switzerland in 1984.

2. I have been employed by Sika Technology AG since 1992 and I have had a total of 18 years of work and research experience in polymer chemistry, particularly in Epoxide and polyurethane chemistry.

3. My publications include the following works in this field: Polymer Chemistry, Epoxide Chemistry, Polyurethane Chemistry, Coatings, Floors, Adhesives.

4. I am a named inventor in the above-captioned patent application.

5. I AM NOT being separately compensated for my work in connection with this Declaration.

6. I have reviewed the application, claims, Office Action, and applied references.

7. Claim 1 requires that the Mannich base has primary amino groups and that the Mannich base is prepared by (1) reacting a phenolic compound of formula (I) with a

formaldehyde in the presence of a tertiary amine, and (2) reacting a resulting product with at least one polyamine.

8. In Example 1 of the specification, a Mannich base was prepared by: (1) reacting 108 g (1 mol) of a phenolic compound of formula (I) (m-cresol) with 72.3 g (2.4 mol) of a formaldehyde (formalin) in the presence of 102 g (1 mol) of a tertiary amine (dimethylaminopropylamine); and (2) reacting a resulting product with 408 g (3 mol) of a polyamine (MXDA). In step (1), the formaldehyde reacts at reactive sites on the phenolic compound and the tertiary amine reacts with the formaldehyde at less than all of the reactive sites by its primary amino group. The resulting product has at least one formaldehyde at reaction sites available for further reaction with a polyamine. The polyamine has at least two primary amino groups. In step (2), a polyamine reacts at such reaction sites of the resulting product of step (1). Thus, the process results in a Mannich base having at least one primary amino group.

9. The Mannich base of Ando was prepared by reacting a phenolic compound, a formaldehyde, and a tertiary amine together in a mixture. The highly reactive formaldehyde reacted at a reactive site on the phenolic compound and the tertiary amine bonded with the formaldehyde, thereby producing the Mannich base. Ando's process does not add a polyamine into the reaction to produce the Mannich base. Once the Mannich base is prepared, Ando teaches that the Mannich base may be mixed with an active amino compound (IV), a polyamine, which is used as a curing agent for epoxy resins. See Ando at col. 14, lines 43-52, and col. 13, lines 43-47. Ando's process does not result in a Mannich base having primary amino groups.

10. The Mannich base prepared from Ando's process does not react with the active amino compound (IV) added to the mixture as a curing agent at a later time. Formaldehyde is required to bond a polyamine to a phenolic compound. If formaldehyde is not present in the

reaction mixture, a polyamine cannot bind to a phenolic compound. With reference to Mannich base (II-b) of Ando's Examples, 130.2 g (1 mol) of diethylaminopropylamine (tertiary amine), 108.1 g (1 mol) of m-cresol (phenolic compound), and 81.1 g of formalin (1 mol formaldehyde) were mixed together in a reaction mixture to produce the Mannich base. Due to the stoichiometry of the reactants, the formaldehyde completely reacts with the m-cresol during Mannich base preparation. Thus, once the active amino compound (IV) is added to the Mannich base mixture to assist in the curing of the epoxy resin, the Mannich base cannot react with the active amino compound (IV) because there is no free formaldehyde respectively bound to the m-cresol as hydroxymethyl groups remaining in the mixture to bond the active amino compound (IV) to a reactive site on the phenolic compound of the Mannich base.

11. Additionally, even in the event that the diethylaminopropylamine does not completely react with the formaldehyde reacted with m-cresol, the formaldehyde and m-cresol intermediate further undergoes a condensation reaction resulting in oligomers known as a formaldehyde/phenol resins. See [http://en.wikipedia.org/phenol\\_formaldehyde\\_resin](http://en.wikipedia.org/phenol_formaldehyde_resin) (attached) as Ando heats up the reaction mixture up to 100 to 150°C during 5 hours. Such undesirable oligomers cannot react with an active amino compound (IV) or a diethylaminopropylamine because the reactive hydroxymethyl groups are no longer present on the oligomers after condensation of the formaldehyde and m-cresol intermediate.

12. Furthermore, due to the highly reactive nature of formaldehydes, it is impossible for any of the formaldehyde to remain unreacted in the mixture after the preparation of the Mannich base. For example, with reference to Mannich base (II-b) of Ando's Examples, the formaldehyde immediately reacts with the m-cresol during the Mannich base preparation process such that no free formaldehyde remains in the mixture after the Mannich base preparation. With reference to Mannich base (II-a) of Ando's Examples, 204.4

g (2 mol) of diethylaminopropylamine (tertiary amine), 94.1 g (1 mol) of phenol (phenolic compound), and 202.7 g of formalin (2.5 mol formaldehyde) were mixed together in a reaction mixture to produce the Mannich base. Even in such a reaction, the free formaldehyde remaining in the mixture after the Mannich base preparation undergoes condensation before the active amino compound (IV) is added to the Mannich base mixture to assist in the curing of the epoxy resin. Thus, no formaldehyde remains in the reaction mixture to react with the active amino compound (IV) after Mannich bases (II-a) or (II-b) are prepared.

13. Therefore, the claimed Mannich base has primary amino groups, whereas the process of preparing a Mannich base disclosed in Ando does not result in a Mannich base having primary amino groups.

14. I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date: Aug. 11, 2010

U. Gerber  
Ulrich GERBER

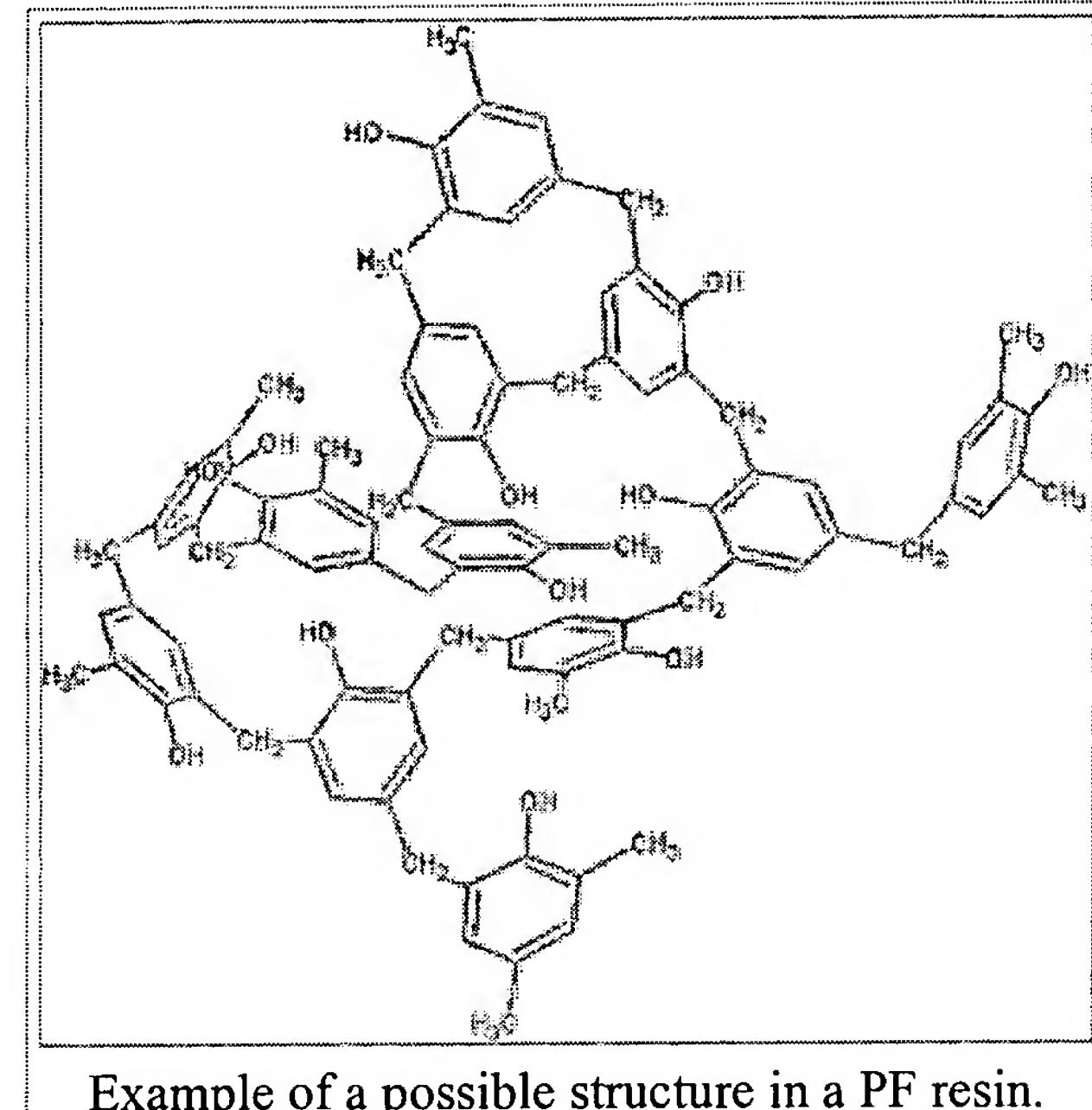
# Phenol formaldehyde resin

From Wikipedia, the free encyclopedia

**Phenol formaldehyde resins** (PF) include synthetic thermosetting resins such as obtained by the reaction of phenols with formaldehyde. Sometimes the precursors include other aldehydes or other phenol. Phenolic resins are mainly used in the production of circuit boards. They are better known however for the production of molded products including pool balls, laboratory countertops, and as coatings and adhesives. In the form of Bakelite, they are the earliest commercial synthetic resin.<sup>[1][2]</sup>

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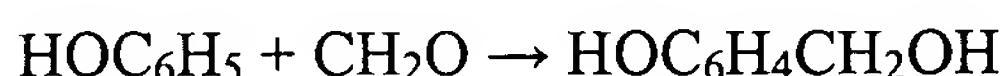


Example of a possible structure in a PF resin.

## Formation and structure

Phenol-formaldehyde resins, as a group, are formed by a step-growth polymerization reaction that can be either acid- or base-catalysed. Since formaldehyde exists predominantly in solution as a dynamic equilibrium of methylene glycol oligomers, the concentration of the *reactive* form of formaldehyde depends on temperature and pH.

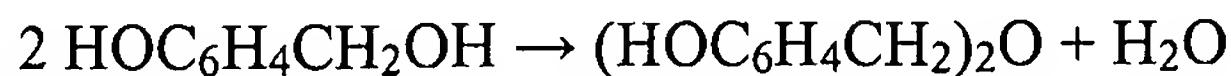
Phenol is reactive towards formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. The initial reaction in all cases involves the formation of a hydroxymethyl phenol:



The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction gives a methylene bridge, and the second forms an ether bridge:



The diphenol  $(\text{HO}\text{C}_6\text{H}_4)_2\text{CH}_2$  (sometimes called a "dimer") is called bisphenol F, which is itself an important monomer in the production of epoxy resins. Bisphenol-F can further link generating tri- and tetra-and higher phenol oligomers.



## Novolac

Novolacs are phenol-formaldehyde resins made where the molar ratio of formaldehyde to phenol of less than one. The polymerization is brought to completion using acid-catalysis. The phenol units are mainly linked by methylene groups. Novolacs are commonly used as photoresists. See also photolithography. The molecular weights are in the low thousands, meaning that about 10-20 phenol units.

Hexamethylene tetramine or "hexamine" is a hardener that is added to crosslink novolac. At  $\geq 180^\circ\text{C}$ , the hexamine forms crosslinks to form methylene and dimethylene amino bridges.

## Resols

Base-catalysed phenol-formaldehyde resins are made with a formaldehyde to phenol ratio of greater than one (usually around 1.5). These resins are called resols. Phenol, formaldehyde, water and catalyst are mixed in the desired amount, depending on the resin to be formed, and are then heated. The first part of the reaction, at around  $70^\circ\text{C}$ , forms a thick reddish-brown tacky material, which is rich in hydroxymethyl and benzylic ether groups.

The rate of the base-catalysed reaction initially increases with pH, and reaches a maximum at about pH = 10. The reactive species is the phenoxide anion ( $\text{C}_6\text{H}_5\text{O}^-$ ) formed by deprotonation of phenol. The negative charge is delocalised over the aromatic ring, activating sites 2, 4 and 6, which then react with the formaldehyde.

Being thermosets, hydroxymethyl phenols will crosslink on heating to around  $120^\circ\text{C}$  to form methylene and methyl ether bridges. At this point the resin is a 3-dimensional network, which is typical of polymerised phenolic resins. The high crosslinking gives this type of phenolic resin its hardness, good thermal stability, and chemical imperviousness.

## Crosslinking and the phenol/formaldehyde ratio

When the molar ratio of formaldehyde:phenol reaches one, in theory every phenol is linked together via methylene bridges, generating one single molecule, and the system is entirely crosslinked. This is why bakelites (F:P < 1) don't harden without the addition of a crosslinking agent, and why resins with the formula F:P > 1 will.

## Applications

Phenolic resins are found in myriad industrial products. Phenolic laminates are made by impregnating one or more layers of a base material such as paper, fiberglass or cotton with phenolic resin and laminating the resin-saturated base material under heat and pressure. The resin fully polymerizes (cures) during this process. The base material choice depends on the intended application of the finished product. Paper phenolics are used in manufacturing electrical components such as punch-through boards

and household laminates. Glass phenolics are particularly well suited for use in the high speed bearing market. Phenolic micro-balloons are used for density control.

## Trade names

- Bakelaque is a rigid laminate or tube made from phenolic resin on a substrate cotton fabric, paper or glass.<sup>[3]</sup>
- Bakelite is made from phenolic resin and wood flour.
- Novotext is cotton fibre-reinforced phenolic, using randomly oriented fibres.
- Paxolin and Richlite are made from phenolic resin and paper.
- Trymer Green is a rigid cellular phenolic thermal insulation.
- Tufnol is made from phenolic resin and woven cotton or linen fabric.<sup>[4]</sup>

## References

1. ^ A. Gardziella, L.A. Pilato, A. Knop, Phenolic Resins: Chemistry, Applications, Standardization, Safety and Ecology, 2nd edition, Springer, 2000
2. ^ Wolfgang Hesse "Phenolic Resins" in Ullmann's Encyclopedia of Industrial Chemistry, 2002, Wiley-VCH, Weinheim. doi:10.1002/14356007.a19\_371 ([http://dx.doi.org/10.1002%2F14356007.a19\\_371](http://dx.doi.org/10.1002%2F14356007.a19_371)).
3. ^ "Attwater Group Industrial Laminates" (<http://www.attwater.com/products/laminate.asp>) . Attwater Group. <http://www.attwater.com/products/laminate.asp>.
4. ^ "TUFNOL Fabric laminates" (<http://www.tufnol.com/tufnol/default.asp?id=21>) . Tufnol. <http://www.tufnol.com/tufnol/default.asp?id=21>.

## External links

- Safety data for phenol-formaldehyde resin ([http://physchem.ox.ac.uk/MSDS/PH/phenol\\_formaldehyde\\_resin.html](http://physchem.ox.ac.uk/MSDS/PH/phenol_formaldehyde_resin.html))

Retrieved from "[http://en.wikipedia.org/wiki/Phenol\\_formaldehyde\\_resin](http://en.wikipedia.org/wiki/Phenol_formaldehyde_resin)"

Categories: Phenolic resins | Plastics | Synthetic resins | Semiconductor device fabrication

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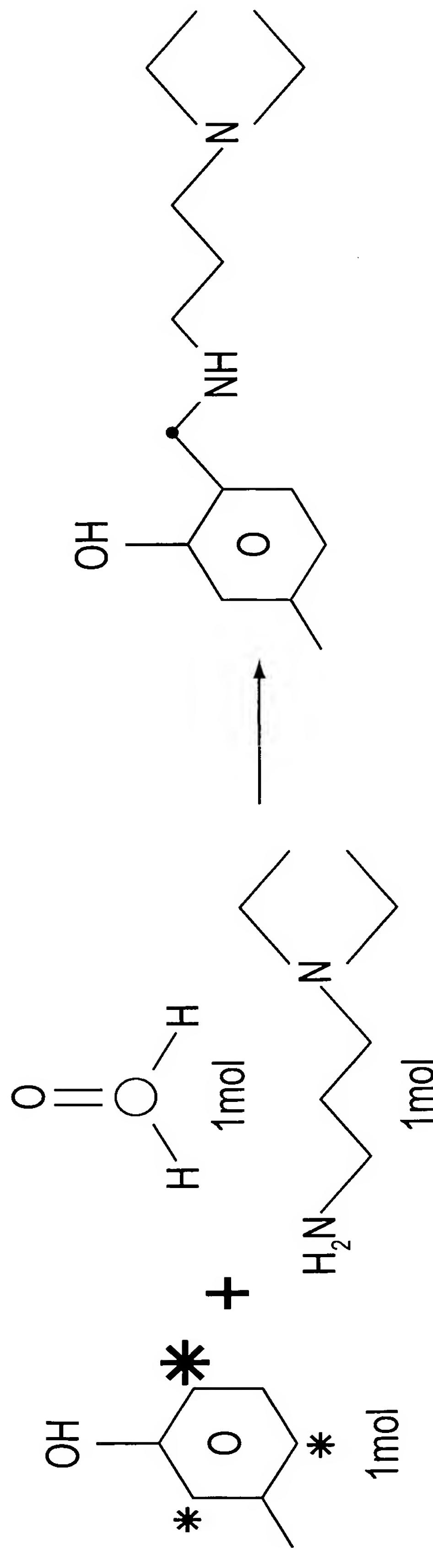
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FIG. 1

Ando

Ando's Mannich Base (II-b)

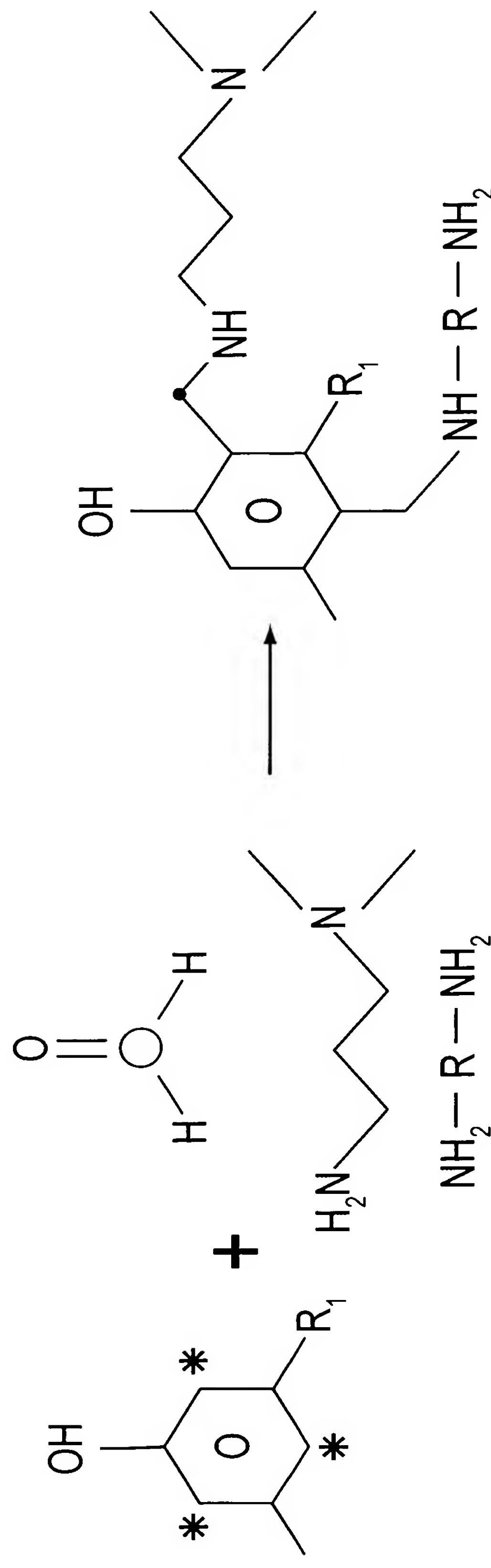


\* = Reactive site

o- & p- sites are accessible for  
substitution (due to steric hindrance  
large \* is the most reactive site)

FIG. 2

Claimed Mannich Base - In the Presence of Tertiary Amines



\* = Reactive site

FIG. 3

Claimed Mannich Base - Example E1

